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Nitride tuning of lanthanide chromites

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Supplementary Information

Experimental Details

The oxynitrides $RCrO_{3-x}N_x$ (R = La, Pr, Nd) were prepared by treatment under NH_3(g) flow of 600 cm^3/min (Carburos Metálicos, 99.9%) of $RCrO_4$ precursor oxides between 700 and 800 ^oC, using several cycles of 10 h with intermediate regrinding. The $RCrO_4$ compounds were prepared using the Pechini method. La_2O_3 (Aldrich, 99.9 %), Pr_6O_{11} (Aldrich, 99.9 %) or Nd_2O_3 (Aldrich, 99.9 %) were first fired at 900 ^oC during 12 hours and dissolved in HNO_3 0.1 M. Then $Cr(NO_3)_3.9H_2O$ (Aldrich 99.99 %), $C_6H_8O_7$ (citric acid, Aldrich 99.5 %) and $C_2H_6O_2$ (ethylene glycol), were subsequently added to the solution in molar ratios R:Cr: $C_6H_8O_7$:$C_2H_6O_2$=1:1:1:1, with continuous stirring and heating at 55-80 ^oC. The solutions were evaporated for 12 h to form the precursor resins that were subsequently treated in air at 540 ^oC for 15 hours.

N contents were determined by combustion analysis in oxygen in a Thermo Fisher Scientific instrument, heating the samples in oxygen up to 1060 ^oC and using MgO, WO_3 and Sn as additives and atropine as a reference standard.

X-ray powder diffraction data were collected on a Siemens D5000 diffractometer using Cu Kα radiation (λ= 1.5418 Å). Synchrotron X-ray powder diffraction data at room temperature were measured from capillary (0.3 mm diameter) samples in the angular range $1.038^o \leq 2\theta \leq 61.09^o$ at the MSPD beamline [1] of the ALBA Synchrotron (Cerdanyola del Vallès, Spain). Using a double Si (111) crystal monochromator, a short wavelength was selected and calibrated with Si NIST (λ = 0.619714 Å). Rietveld analysis was carried out using the program Fullprof.[2] Background refinement was performed by linear interpolation and the data were corrected for absorption.

Room temperature neutron powder diffraction data for $LaCrO_{2.72}N_{0.28}$ was collected on the D2B diffractometer at the Institut Laue-Langevin (ILL), Grenoble using 450 mg of sample placed in a 5 mm diameter vanadium can. The neutron wavelength was 1.594 Å. Room temperature data was collected for $NdCrO_{2.58}N_{0.42}$ and $PrCrO_{2.64}N_{0.36}$ on the D20 diffractometer also at the Institut Laue-Langevin. The neutron wavelength was 1.36 Å using a take-off angle of 118^o. Low temperature neutron powder diffraction was carried out on all the samples on D1B diffractometer at the ILL. The neutron wavelength was 2.524 Å. For the R= La and Nd samples a series of scans were taken at intervals of approximately 6.5 K between 10 K – 315 K for R= La and approximately 3.5 K between 1.5 K- 215 K for R= Nd. For R= Pr, data was collected in 50 K intervals between 1.5 K and 250 K. Powder diffraction data were analysed using the FullProf software package. [2] The anion composition of the oxynitrides was constrained by the chemically determined value.

Magnetic measurements were performed between at H=2000 G between 10 K and 400 K using a Quantum Design SQUID magnetometer.

Table S1. Summary of the P*bnm* model for $LaCrO_{2.72}N_{0.28}$ refined against room temperature synchrotron X-ray powder diffraction data. Refined cell parameters: a=5.52201(4), b=5.48192(5), c=7.6573(7) Å. R_{wp} = 4.33 %, χ^2 = 8.21 for 59 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
La	4c	0.9978(2)	0.01274(9)	1/4	0.715(6)
Cr	4b	1/2	0.0	0.0	0.344(8)
X1	4b	0.070(1)	0.493(1)	1/4	0.31(4)
X2	8d	0.727(1)	0.268(1)	0.0353(5)	0.31(4)

	La-X1	**La-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.391(6)	2.474(5) × 2	1.980(1) × 2	1.953(6) × 2
	2.660(6)	2.640(6) × 2		1.989(6) × 2
	2.879(6)	2.821(5) × 2		
	3.136(6)	3.096(5) × 2		

	Cr-X1-Cr	**Cr-X2-Cr**
Bond Angle / °	157.45(5)	161.5(3)

Table S2. Summary of the P*bnm* model for $PrCrO_{2.81}N_{0.19}$ refined against room temperature synchrotron X-ray powder diffraction data. Refined cell parameters: a= 5.45535(4), b= 5.49076(3), c= 7.72751(5) Å. R_{wp} = 3.24 %, χ^2 = 3.93 for 55 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
Pr	4c	0.9932(1)	0.03577(4)	1/4	0.610(4)
Cr	4b	1/2	0.0	0.0	0.158(8)
X1	4b	0.0736(9)	0.4815(5)	1/4	0.25(6)
X2	8d	0.7147(7)	0.2939(6)	0.0388(5)	0.25(6)

	Pr-X1	**Pr-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.382(5)	2.390(4) × 2	1.976(1) × 2	1.948(4) × 2
	2.486(3)	2.642(4) × 2		2.016(3) × 2
	3.075(3)	2.705(4) × 2		
	3.107(5)	3.286(4) × 2		

	Cr-X1-Cr	**Cr-X2-Cr**
Bond Angle / °	155.80(4)	155.0(2)

Table S3. Summary of the P*bnm* model for $NdCrO_{2.58}N_{0.42}$ refined against room temperature synchrotron X-ray powder diffraction data. Refined cell parameters: a=5.42787(3), b=5.50102(3), c=7.70936(4) Å. R_{wp} = 2.36 %, χ^2 = 7.72 for 96 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
Nd	4c	0.9919(1)	0.04131(5)	1/4	0.787(7)
Cr	4b	1/2	0.0	0.0	0.17(1)
X1	4b	0.0851(9)	0.484(7)	1/4	0.53(4)
X2	8d	0.7190(7)	0.2935(7)	0.0410(5)	0.43(4)

	Nd-X1	**Nd-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.318(5)	2.401(4) × 2	1.984(1) × 2	1.928(4) × 2
	2.487(3)	2.591(4) × 2		2.030(4) × 2
	3.108(3)	2.716 (4) × 2		
	3.148(5)	3.300 (4) × 2		
	Cr-X1-Cr	**Cr-X2-Cr**		
Bond Angle / °	152.57(5)	155.0(2)		

Table S4. Summary of the P*bnm* model for $LaCrO_{2.72}N_{0.28}$ refined against room temperature neutron powder diffraction data. Refined cell parameters: a=5.5237(2), b=5.4787(2), c=7.7684(2) Å. R_{wp} = 2.45 %, χ^2 = 1.89 for 41 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
La	4c	0.0037(8)	0.0152(7)	1/4	0.038(4)
Cr	4b	1/2	0.0	0.0	0.036(5)
X1	4b	0.0671(7)	0.487(1)	1/4	0.732(4)
X2	8d	0.7325(7)	0.2705(7)	0.0362(3)	0.732(4)

	La-X1	**La-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.376(6)	2.502(4) × 2	1.978(8) × 2	1.961(4) × 2
	2.613(8)	2.638(5) × 2		1.981(4) × 2
	2.911(8)	2.814(4) × 2		
	3.156(6)	3.085(4) × 2		
	Cr-X1-Cr	**Cr-X2-Cr**		
Bond Angle / °	158.05(3)	161.5(2)		

Table S5. Summary of the P*bnm* model for $PrCrO_{2.64}N_{0.36}$ refined against room temperature neutron powder diffraction data. Refined cell parameters: a= 5.3976(2), b= 5.4336(2), c= 7.6461(3) Å. R_{wp} = 1.40 %, χ^2 = 1.82 for 128 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
Pr	4c	0.9959(2)	0.0302(8)	1/4	0.341(7)
Cr	4b	1/2	0.0	0.0	0.599(4)
X1	4b	0.0756(9)	0.4843(7)	1/4	0.599(4)
X2	8d	0.7106(5)	0.2904(5)	0.0403(4)	0.599(4)

	Pr-X1	**Pr-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.326(1)	2.348(6) × 2	1.956(1) × 2	1.958(3) × 2
	2.504(6)	2.635(7) × 2		1.969(3) × 2
	2.997(6)	2.687(5) × 2		
	3.095(1)	3.236(6) × 2		

	Cr-X1-Cr	**Cr-X2-Cr**
Bond Angle / °	155.4(4)	154.5(1)

Table S6. Summary of the P*bnm* model for $NdCrO_{2.58}N_{0.42}$ refined against room temperature neutron powder diffraction data. Refined cell parameters: a=5.3715(2), b=5.4459(2), c=7.6316(2) Å. R_{wp} = 1.36 %, χ^2 = 2.07 for 93 variables.

Atom	**Site**	**x**	**y**	**z**	**B_{iso} (Å^2)**
Nd	4c	0.9930(9)	0.0388(5)	1/4	0.182(3)
Cr	4b	1/2	0.0	0.0	0.182(3)
X1	4b	0.0796(8)	0.4800(7)	1/4	0.897(4)
X2	8d	0.7097(5)	0.2944(5)	0.0421(4)	0.897(4)

	Nd-X1	**Nd-X2**	**Cr-X1**	**Cr-X2**
Bond length / Å	2.319(6)	2.340(4) × 2	1.958(1) × 2	1.946(3) × 2
	2.447(5)	2.602(4) × 2		1.985(3) × 2
	3.078(5)	2.674(4) × 2		
	3.092(6)	3.288(4) × 2		

	Cr-X1-Cr	**Cr-X2-Cr**
Bond Angle / °	153.99(4)	153.16(1)

Table S7. Summary of the magnetic refinements for P*bnm* models at base temperatures using D1B neutron diffraction data. Refined lattice parameters and ordered moments at Cr and Nd sites are shown.

Sample	T/K	a/Å	b/Å	c/Å	μ_y(Cr)/ μ_B	μ_z(Ln)/ μ_B
$LaCrO_{2.72}N_{0.28}$	10	5.4508(9)	5.4086(6)	7.666(2)	2.73(5)	
$PrCrO_{2.64}N_{0.36}$	1.5	5.3258(7)	5.4039(7)	7.575(1)	2.60(8)	
$NdCrO_{2.58}N_{0.42}$	1.5	5.3569(7)	5.3922(6)	7.598(1)	2.59(5)	1.4(1)

Table S8 Values of Curie temperatures and other magnetic parameters from Curie-Weiss fits to data above T_C for Ln = Pr and Nd samples (this was not possible for Ln = La due to the high T_C). Effective Cr paramagnetic moments were estimated by subtracting the ideal Ln^{3+} contribution from the total as shown in the Table footnote.

Ln, x[a]	T_C/K	T_{SR}/K	θ/K	μ_{eff}/μ_B	$\mu_{eff}(Cr)/\mu_B$[a]
La, 0	293				
La, 0.11	285				
La, 0.17	283				
La, 0.21	283				
La, 0.25	280				
La, 0.28	281				
Pr, 0	240	-	-217	5.50	4.17
Pr, 0.19	229	-	-156	5.17	3.73
Pr, 0.36	232	-	-43	4.30	2.38
Nd, 0	226	28	-251	4.72	3.03
Nd, 0.35	210	44	-138	5.21	3.75
Nd, 0.59	214	-	-91	4.60	2.84

[a] $\mu_{eff}(Cr) = [\mu_{eff}^2 - \mu_{eff}(Ln^{3+})^2]^{1/2}$ where $\mu_{eff}(Pr^{3+}) = 3.58$ and $\mu_{eff}(Nd^{3+}) = 3.62\ \mu_B$.

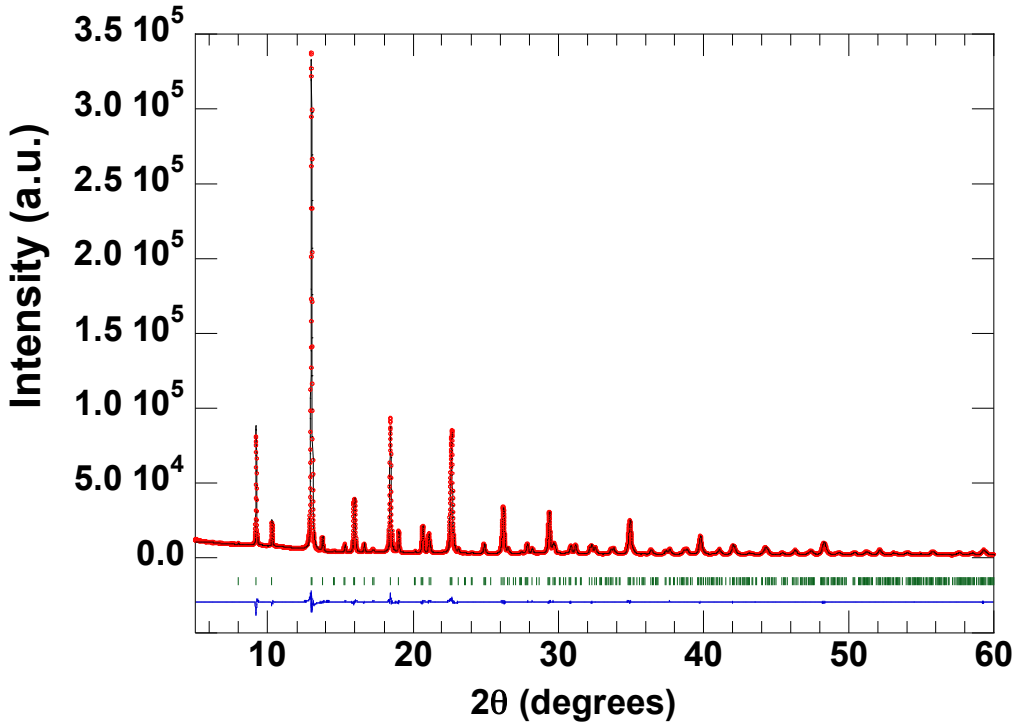

Figure S1. Observed and calculated synchrotron X-ray powder diffraction patterns for $PrCrO_{2.81}N_{0.19}$.

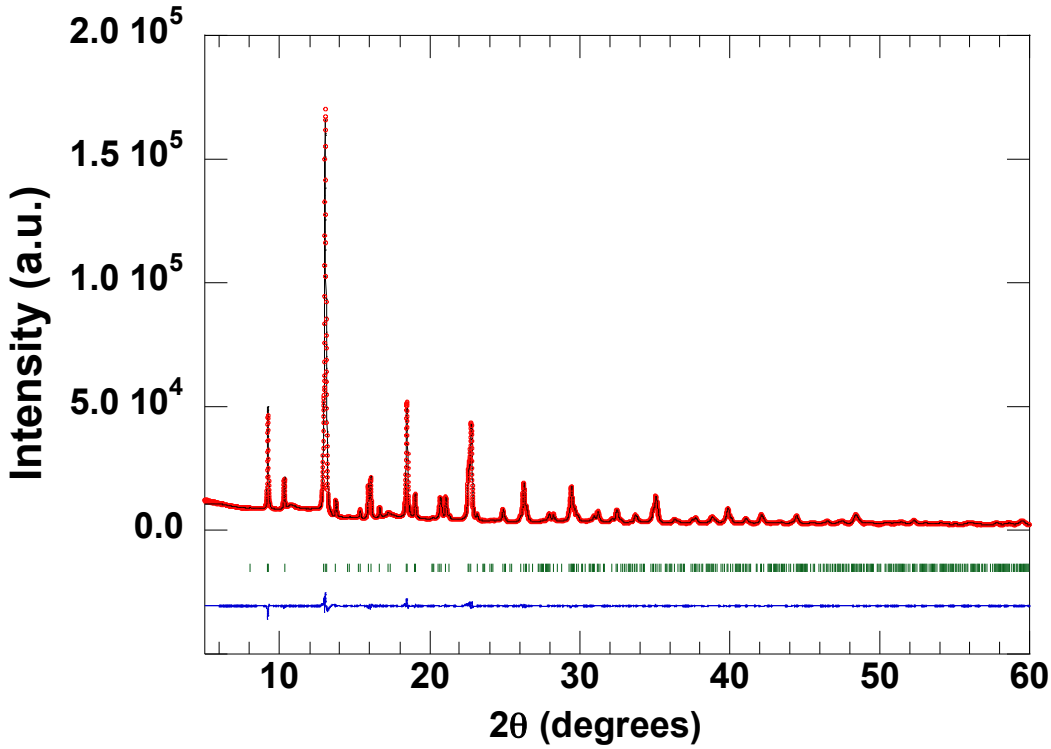

Figure S2. Observed and calculated synchrotron X-ray powder diffraction patterns for $NdCrO_{2.58}N_{0.42}$.

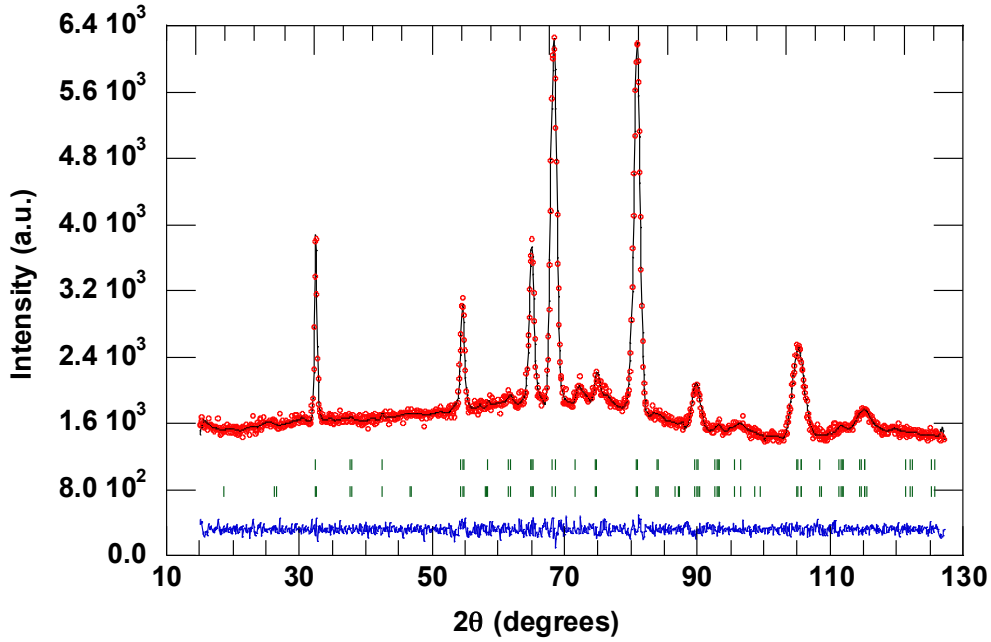

Figure S3. Observed and calculated 10 K neutron powder diffraction patterns for $LaCrO_{2.72}N_{0.28}$ (λ=2.524 Å).

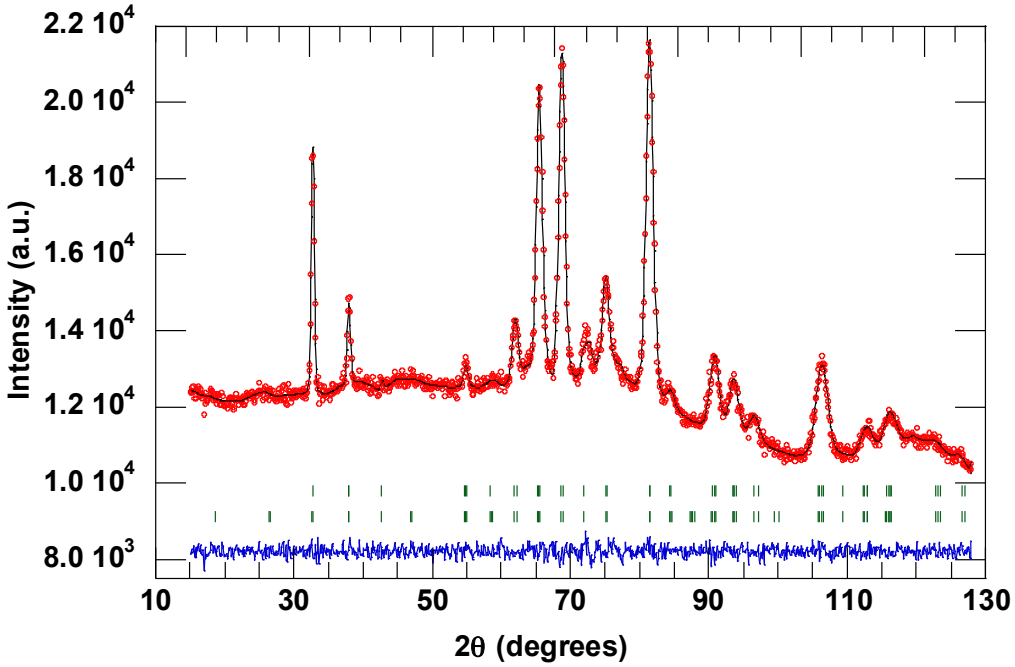

Figure S4. Observed and calculated 1.5 K neutron powder diffraction patterns for $PrCrO_{2.64}N_{0.36}$ (λ=2.524 Å).

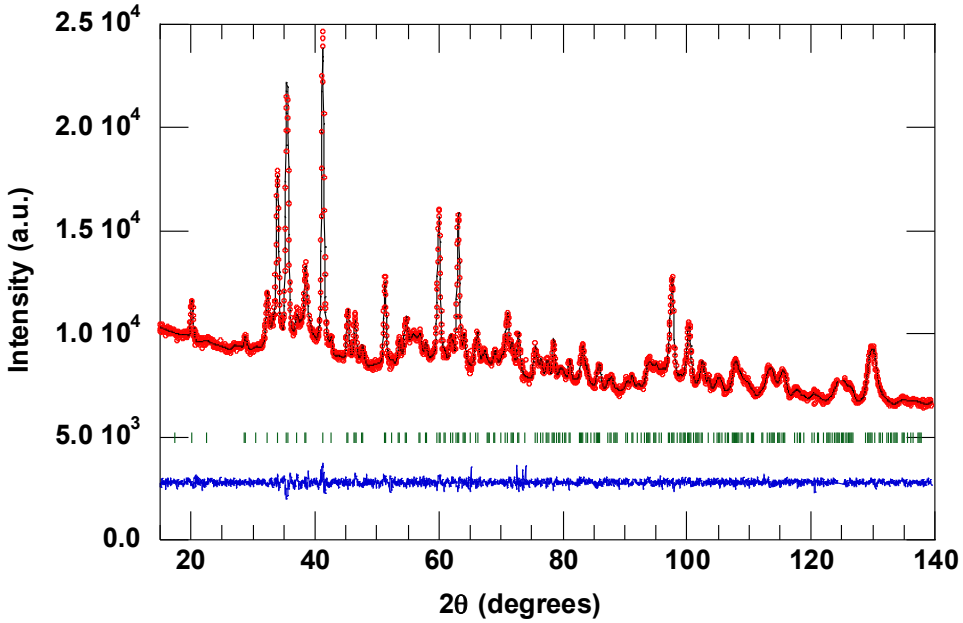

Figure S5. Observed and calculated room temperature neutron powder diffraction patterns for $PrCrO_{2.64}N_{0.36}$ (λ= 1.36 Å)

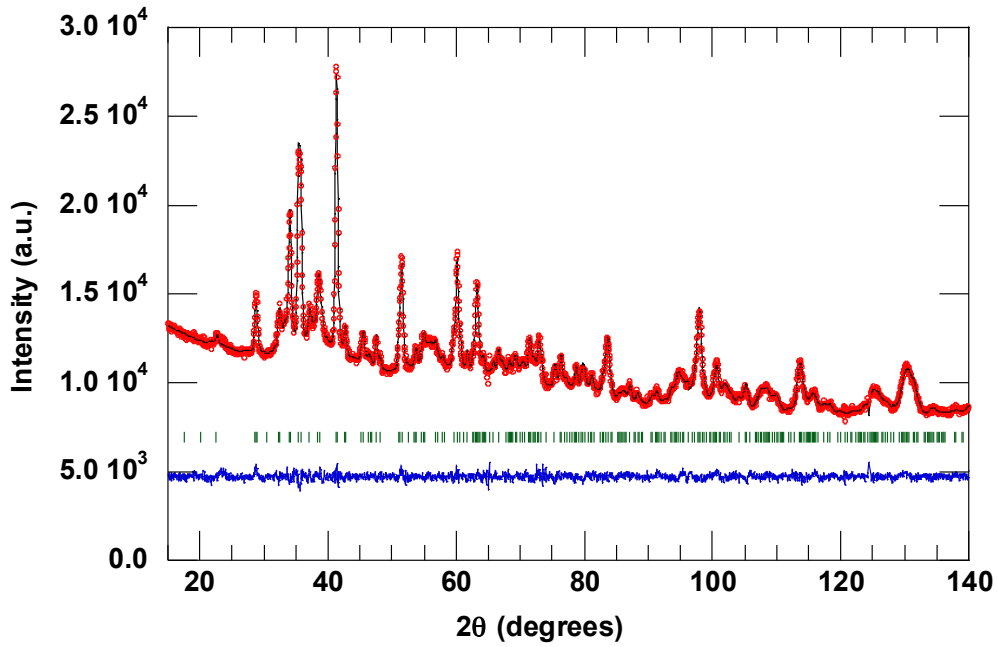

Figure S6. Observed and calculated room temperature neutron powder diffraction patterns for $NdCrO_{2.58}N_{0.42}$ (λ=1.36 Å).

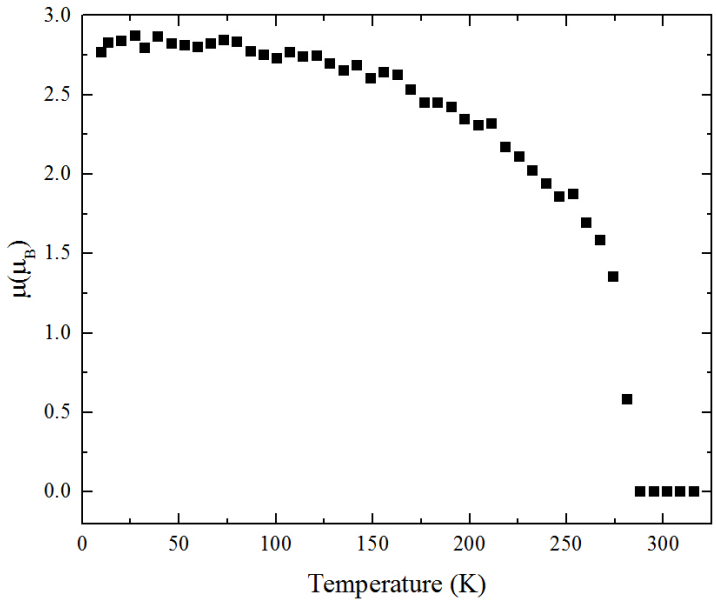

Figure S7. Thermal variation of refined Cr magnetic moment for $LaCrO_{2.72}N_{0.28}$.

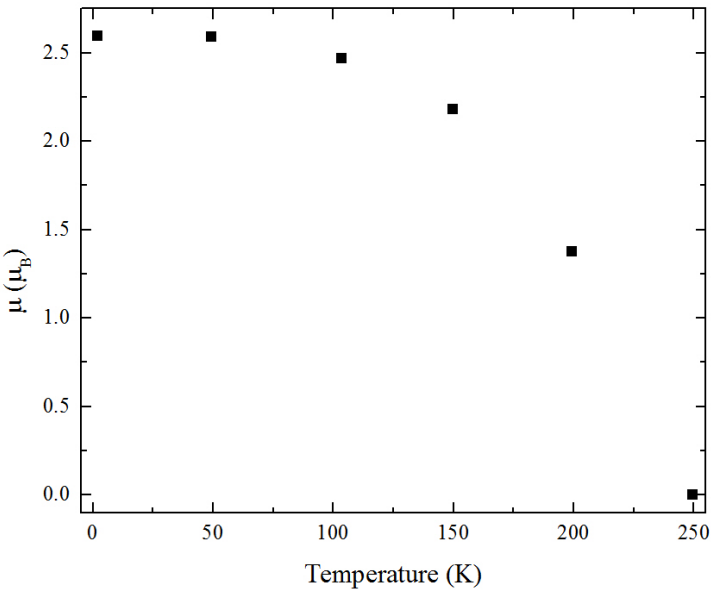

Figure S8. Thermal variation of refined Cr magnetic moment for $PrCrO_{2.64}N_{0.36}$.

[1] F. Fauth, I. Peral, C. Popescu, C. and M. Knapp, M. *Powder Diffraction* **28**, S360–S370 (2013).

[2] J.Rodríguez-Carvajal, *Phys. B*, 1993, **192**, 55.